Giant isotope effect and spin state transition induced by oxygen isotope exchange in $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$

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We systematically investigate effect of oxygen isotope in $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ which shows a crossover with x from ferromagnetic metal to the insulator with spin-state transition. A striking feature is that effect of oxygen isotope on the ferromagnetic transition is negligible in the metallic phase, while replacing ^{16}O with ^{18}O leads to a giant up-shift of the spin-state transition temperature (T_s) in the insulating phase, especially T_s shifts from 36 to 54 K with isotope component $\alpha_S = -4.7$ for the sample with x=0.175. A metal-insulator transition is induced by oxygen isotope exchange in the sample x=0.172 being close to the insulating phase. The contrasting behaviors observed in the two phases can be well explained by occurrence of static Jahn-Teller distortions in the insulating phase, while absence of them in the metallic phase.

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Cobaltites with CoO_6 octahedra have recently attracted much attention because they exhibit various intriguing physical properties as magnetoresistance,[1] enormous Hall effect,[2] superconductivity,[3] and large thermoelectric effect.[4] Provskite-related cobalt oxides show their unique feature: temperature-induced spin state transition (SST).[5, 6] Such spin state transition, which is extremely sensitive to composition and pressure,[7] is closely connected with electrical conductivity. The Co^{3+} ion, which contains six 3d electrons, often exhibits a SST from the low spin (LS, t_{2g}^6) ground state to the intermediate spin (IS, $t_{2g}^5 e_g^1$) or to the high spin (HS, $t_{2g}^4 e_g^2$) state with increasing temperature. The most important character of the SST in perovskite-type cobalt oxides is often accompanied by the metal-insulator transition (MIT).

Experimental and theoretical works indicated that the spin-state transition in cobaltites is from LS to IS below room temperature.[6, 8, 9, 10] The IS state is expected to be strong Jahn-Teller (JT) active due to the partially filled e_g level, creating monoclinic distortions of CoO_6 octahedra. Actually, elastic and inelastic neutron scattering showed that spin activation of Co^{+3} ions in $La_{1-x}Sr_xCoO_3$ system induces local static JT distortions in the paramagnetic insulating phase for all x, while the static JT distortions are absent in the ferromagnetic metal phase.[11] Understanding the characteristics of Jahn-Teller instability can help elucidate the nature of metal-insulator transition, magnetoresistance, and even superconductivity.[12] The IS-JT state is stabilized with doping in the insulating phase for perovskite cobalt oxides.[6, 13] However, charge dynamics interfere with orbital JT ordering resulting in a new state and the JT distortions can lose their long-range coherency with increasing charge mobility in the ferromagnetic metal phase. JT interactions in perovskite oxides often result in quite intriguing physical phenomena through the coupling between orbital and spin degrees of freedom with lattice.[14] Coupling of JT modes to the lattice results in formation of small JT polarons, so that coupling of the charge carrier to the JT lattice distortions leads to a giant oxygen isotope effect, and the JT distortions play an essential role in $La_{1-x}Ca_xMnO_{3+y}$.[15] Especially, a metal-insulator transition was induced by oxygen isotope exchange in $La_{0.175}Pr_{0.525}Ca_{0.3}MnO_3$.[16] To investigate JT physics and its role played in cobaltites, here we systematically study effect of oxygen isotope in perovskite $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ system with different x. This system is suitable to study the JT physics by oxygen isotope effect since it shows a crossover at x~0.175 from a *ferromagnetic metal phase* to *an insulating phase* with SST with increasing x.[17, 18] Therefore, it is expected that effect of oxygen isotope should be quite different in the ferromagnetic metal phase from in the insulating phase because the static JT distortions are observed in the insulating phase, while absent in the metallic phase.

Polycrystalline samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with different x were prepared by conventional solid-state reaction. Proper molar ratios of Pr_6O_{11}, Sm_2O_3, $CaCO_3$ and Co_3O_4 were mixed, well ground and then calcined at 1000 ^oC and 1100 ^oC for 24 h with intermittent grinding. The pellets pressed from the powder were sintered at 1200 ^oC in the flowing oxygen for 48 h. All samples were characterized by X-ray diffraction and found to be single phase. One pellet for the samples with different x obtained above was cut into two pieces for oxygen-isotope diffusion. The two pieces for each composition were put into an alumina boat which were sealed in a quartz tube filled with oxygen pressure

of 1 bar (one for ^{16}O and another for ^{18}O) mounted in a furnace, respectively. The quartz tubes formed parts of two identical closed loops. They were heated at 1000 ^oC for 48 h and then slowly cooled to room temperature. The obtained samples were re-examined by X-ray diffraction to confirm them single phase. The oxygen-isotope enrichment is determined from the weight changes of both ^{16}O and ^{18}O samples. The ^{18}O samples have about 70% ^{18}O and 30% ^{16}O. To make sure the isotope exchange effect, back-exchange of ^{18}O sample by ^{16}O was carried out in the same way and the weight change showed a complete back-exchange. Magnetic susceptibility measurements were performed with a SQUID magnetometer in a magnetic field of 1000 Oe. Resistance measurements were performed using the ac four-probe method with an ac resistance bridge system (Linear Research Inc. LR-700P).

Figure 1 shows temperature dependence of resistivity for the samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with x=0.175, 0.20, 0.25 and 0.30 treated in ^{16}O and ^{18}O, respectively. The samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with various x treated in ^{16}O shows a very weak semiconductive behavior at the high temperatures, while a sharp metal-insulator transition is observed at certain temperatures (T_S) for different x with decreasing temperature. T_S increases with increasing x. As shown in Fig.1, substitution of ^{18}O for ^{16}O leads to an enhancement of T_S for all samples. The up-shift of T_S decreases with increasing x. A giant isotope shift is observed in the sample with x=0.175. T_S shifts from 36 to 54 K after replacing of ^{16}O by ^{18}O. The oxygen isotope exponent $\alpha_s = -dlnT_S/dlnM_O$ (where M_O is the oxygen isotope mass) is about -4.7, which is much larger than $\alpha_c = 0.8$
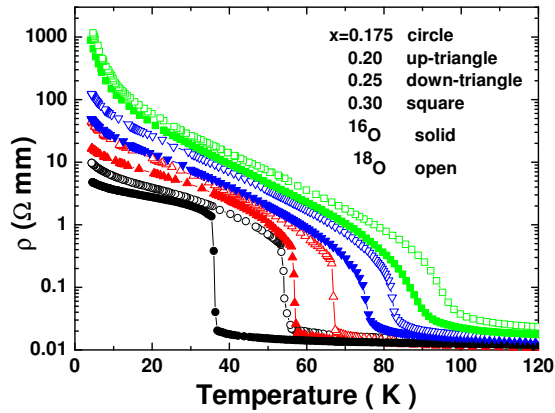
observed in $La_{1-x}Ca_xMnO_{3+y}$.[15] However, the up-shift of T_S is about 7 K for the sample with x=0.30 and the isotope component α_s is about -0.8. To make sure that the effect arises from the oxygen isotope exchange, we carried out the isotope back-exchange. The transport properties completely return to that observed in the samples previously treated in ^{16}O and ^{18}O after the isotope back-exchange, respectively. Such metal-insulator transition has been believed to arise from the spin-state transition. Therefore, the susceptibility was measured for the samples above.

Temperature dependence of susceptibility measured in the field-cooled process with magnetic field of 1000 Oe is shown in Fig.2 for the same samples used in resistivity measurements. All samples show a sharp SST from IS state to LS state with decreasing temperature, respectively. T_s increases with increasing x. Replacing of ^{16}O with ^{18}O makes T_s shift to high-temperature. This is consistent with metal-insulator transition observed in resistivity as shown in Fig.1. It should be pointed out that T_s is exactly the same as that of metal-insulator transition observed in Fig.1. The sample with x=0.175 treated in ^{16}O and ^{18}O show a sharp SST from IS state to LS state with decreasing temperature at 36 and 54 K, respectively. It further supports that the metal-insulator transition arises from the SST. It has been noted that there exists a thermal hysteresis for the phase transition. Therefore, all measurements were carried out in the cooled process to keep the consistency.

Figure 3 shows temperature dependences of resistivity and susceptibility for the ^{16}O and ^{18}O samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with x=0.172. The sample treated in ^{16}O shows a very weak semiconductive be-

FIG. 1: Temperature dependence of resistivity for the ^{16}O and ^{18}O samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with x=0.175, 0.20, 0.25 and 0.30. The data denoted by the solid and open symbols are taken from the samples treated in ^{16}O and ^{18}O, respectively.
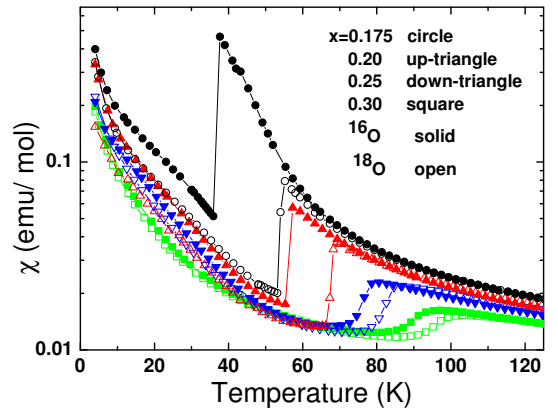

FIG. 2: Temperature dependence of susceptibility for the ^{16}O and ^{18}O samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with x=0.175, 0.20, 0.25 and 0.30. The data denoted by the solid and open symbols are taken from the samples treated in ^{16}O and ^{18}O, respectively.
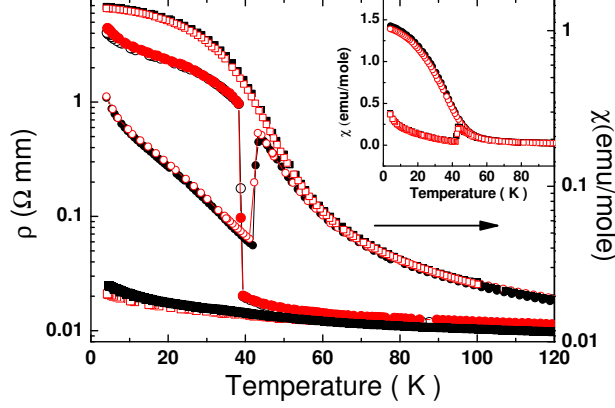
FIG. 3: Temperature dependences of resistivity and suscepti-bility for the sample $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with x=0.172 (solid squares for the ^{16}O sample; solid circles for ^{18}O sample). The data denoted by the open symbols were obtained after the oxygen isotope back-exchange ($^{16}O \rightarrow^{18}O$ and $^{18}O \rightarrow^{16}O$). The reversibility of the metal-insulator transition induced by oxygen isotope exchange is clear.

havior at the low temperatures and no phase transition, while a sharp metal-insulator transition is observed at about 39 K after the treatment in ^{18}O. It suggests that a metal-insulator transition is induced by oxygen isotope exchange. To make sure that the effect arises from the oxygen isotope exchange, we carried out the isotope back-exchange. As shown in Fig.3, the transport properties completely return to that observed in the samples pre-viously treated in ^{16}O and ^{18}O after the isotope back-exchange, respectively. The remarkable feature is that the metal-insulator transition disappears after the sub-sequent treatment in ^{16}O, while shows up after the sub-sequent treatment in ^{18}O. It definitely indicates that the metal-insulator transition is induced by replacing ^{16}O with ^{18}O.

As shown in Fig.3, a striking feature for susceptibil-ity is that the sample $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with x=0.172 treated in ^{16}O shows a ferromagnetic transition at about 60 K, while the ferromagnetic transition disap-pears and a sharp spin-state transition at about 42 K is induced after replacing of ^{16}O with ^{18}O. To clearly show a ferromagnetic transition, the same data are plot-ted with linear vertical axis in the inset of Fig.3. It indi-cates that the replacement of ^{16}O with ^{18}O suppresses the ferromagnetic phase, while induces a SST in the sample with x=0.172. It suggests that there exists a competi-tion between the ferromagnetic transition and SST. This result is consistent with that observed in resistivity mea-surements. It should be pointed out that the transition temperature in susceptibility is about 3 K higher than that in resistivity, in contrast to the case for samples with $x \geq 0.175$. The isotope back-exchange results fur-

ther confirm that the behavior observed in Fig.3 is due to oxygen isotope exchange. Beyond the expectation, a phase transition from ferromagnetic metal to an insu-lator with spin-state transition is induced by replacing replacing ^{16}O with ^{18}O.
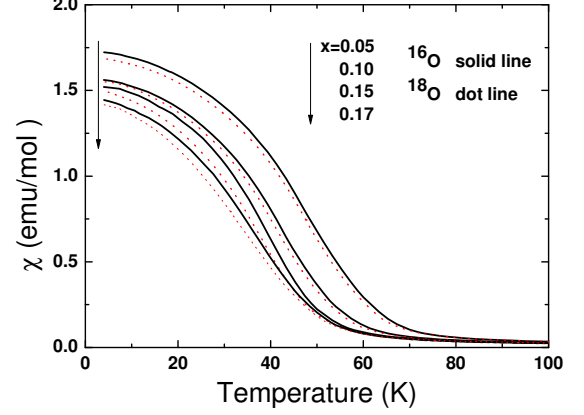

FIG. 4: Temperature dependence of susceptibility for the ^{16}O and ^{18}O samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with x=0.05, 0.10, 0.15 and 0.17: solid lines for ^{16}O samples; dot lines for ^{18}O samples.

To further study the JT physics by oxygen isotope ef-fect in the ferromagnetic metal phase, the susceptibility is systematically studied on the ^{16}O and ^{18}O samples $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with x=0.05, 0.10, 0.15 and 0.17. Temperature dependence of susceptibility for these samples are shown in Fig.4. Actually, substitution of ^{18}O for ^{16}O suppresses the ferromagnetic transition and leads to a down-shift of the Curie temperature (T_c), being sim-ilar to that observed in mamganites although the down-shift of T_c is much less relative to $La_{1-x}Ca_xMnO_{3+y}$.[15] The down-shift of T_c slightly increases with increasing x. However, the shift of T_c is very small compared to that of T_S. It suggests that the effect of oxygen isotope on ferromagnetic transition is negligible.

In order to compare the effect of oxygen isotope in the ferromagnetic metallic phase and in the insulating phase with spin-state transition, the isotope components α_s for SST and α_c for ferromagnetic transition as a function of x and the average ionic radius of A site are shown in Fig.5. The isotope component α_s decreases with increas-ing Sm content x in $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ system. As observed in Fig.1 and Fig.2, T_S increases with in-creasing x, while its isotope shift ΔT_s decreases. There-fore, it leads to a decrease of the isotope component α_s with increasing x. Substitution of ^{16}O by ^{18}O leads to a decrease in the Curie temperature (T_c) although its oxygen isotope shift is negligible. Its isotope component α_c is positive and increases with increasing x, in con-trast to the α_s. It further confirms that there exists a
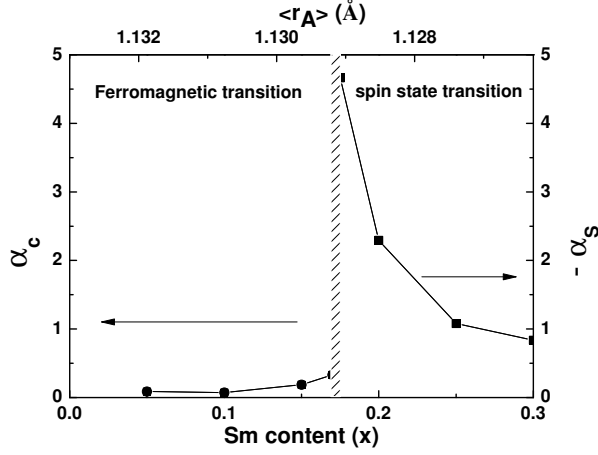
FIG. 5: The oxygen isotope exponent α_c and α_s as a function of Sm content x and the average ionic radius $< r_A >$ of A site $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}$ in $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ system.

competition between ferromagnetic transition and SST. As shown in Fig.5, a maximum isotope component α is observed in the boundary between ferromagnetic metal and insulating phases. A intriguing phenomenon is that the substitution of ^{16}O by ^{18}O leads to a disappearance of ferromagnetic transition and induces the SST accompanied by the metal-insulator transition in the sample $(Pr_{0.828}Sm_{0.172})_{0.7}Ca_{0.3}CoO_3$ which is in the ferromagnetic metal phase close to the crossover boundary.

In the insulating regime (x>0.175), the up-shift of T_S induced by oxygen isotope exchange can be explained to originate from that substitution of ^{16}O by ^{18}O leads to a decrease in frequency of phonon, and consequently enhances effective mass of electron (m^*) through strong electron-phonon coupling. The enhancement of m^* leads to a decrease of bandwidth W, resulting in an increase of energy difference ΔE between IS and LS states and consequently an up-shift of T_s. The increase of Sm-doping leads to a decrease in the ionic radius of A site $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}$ in the $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ system, so that volume of the CoO_6 octahedra decreases. The decrease in volume of the CoO_6 octahedra results in an increase of crystal field splitting energy Δ_C and ΔE, causing an increase in T_S. Therefore, decrease of the isotope component α_s with increasing x could be due to the increase of T_s. In contrast to the giant oxygen isotope effect in the insulating phase, a negligible oxygen isotope effect on T_c is observed in the ferromagnetic metal regime. It has been reported that substitution of ^{16}O by ^{18}O leads to a giant down-shift of Curie temperature in $La_{1-x}Ca_xMnO_{3+y}$.[15] Such giant oxygen isotope shift was explained by the JT polaron formed due to strong Jahn-Teller effect.[15] Recently, elastic and inelastic neutron scattering showed that spin activation of Co^{+3} ions in perovskite cobalt oxides induces local static JT distortions in the insulating phase, while the static JT dis-

tortions are absent in the ferromagnetic metal phase.[11] This observation explained that the giant oxygen isotope effect is observed in the insulating phase, while negligible in the ferromagnetic metal phase well. The lattice distortions from the JT effect with strong electron-phonon coupling should be responsible for the giant isotope effect in the insulating phase.

In conclusion, oxygen isotope effect is systematically studied in $(Pr_{1-x}Sm_x)_{0.7}Ca_{0.3}CoO_3$ with a crossover at x~01.75 from a ferromagnetic metal to an insulating phase with SST. A giant oxygen isotope effect is observed in the insulating phase with an isotope component $\alpha_S = -4.7$ for the sample with x=0.175 which is significantly larger than that found for any magnetic or electronic phase transition in other oxides, while a negligible oxygen isotope effect occurs in the ferromagnetic metal phase. Beyond the expectation, substitution of ^{16}O by ^{18}O leads to a phase transition from a ferromagnetic metal to an insulator in the sample with x=0.172 which lies in the ferromagnetic metal phase close to the crossover boundary. These contrasting behaviors are in support of the observation that static JT distortions occurs in the insulating phase, while are absent in the ferromagnetic metal phase.[11] It provides a direct demonstration of the important of lattice vibrations in these materials.

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